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Research Article

Electrochemical performance of Ti_3C_2 supercapacitors in KOH electrolyte

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Abstract: Two-dimensional (2D) carbide Ti_3C_2 was synthesized by exfoliating Ti_3AlC_2 in HF solution and used for supercapacitive performance investigation in 3 M KOH electrolyte. The specific surface area (SSA) of as-synthesized Ti_3C_2 was 22.35 m^2/g. Ti_3C_2-based supercapacitor electrodes exhibited good energy storage ability and had a volumetric capacitance 119.8 F/cm^3 at the current density of 2.5 A/g. Moreover, the addition of carbon black into Ti_3C_2 powders greatly improved the performance of Ti_3C_2-based capacitors because carbon black restrained the preferred orientation of 2D Ti_3C_2, providing fast ion transport channels, and in turn, decreasing electrical resistance from 16.7 Ω to 3.5 Ω.

Keywords: MXene; Ti_3AlC_2; two-dimensional (2D) carbide; supercapacitors

1 Introduction

Supercapacitors have fast charge/discharge rates, high power density, and good cyclability compared with batteries, and have attracted extensive research interest due to the increasing demand for portable and clean energy storage devices. In principle, supercapacitors store charges at the interface between electrode and electrolyte, thus large specific surface area (SSA) of electrode is favorable for high capacitance [1]. Therefore, many materials with large SSA were used as electrode, such as activated carbons [2,3], carbide-derived carbons [4,5], and carbon nanotubes [6,7]. Two-dimensional (2D) materials prepared by exfoliating precursors with layered structure [8,9] have high SSA, which are regarded as one of promising candidates for supercapacitor electrodes. The first and most investigated 2D material is graphene. Graphene or graphene-based electrodes for supercapacitors have been successfully prepared and their supercapcitor performance has been investigated extensively [10–13].

Recently, a new family of 2D materials was prepared by exfoliating ternary carbides or carbonitrides with the name of MAX phases [14,15]. The 2D materials were named as MXene to emphasize their graphene-like structure and the removing of A-site atoms from MAX structure. MAX phases, the precursors of MXenes, have the general formula of $M_{n+1}AX_n$, where M is an early transition metal; A is an A-group element (mostly group IIIA or IVA); and X is either carbon or nitrogen [16,17].

MXenes have important application in many areas, such as hydrogen storage [18,19], lead adsorption [20], and catalysis [21]. Especially, as conductive and hydrophilic 2D materials [14], MXenes are promising electrode materials for electrochemical energy storage

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[22–25]. Ti_3C_2 is a typical MXene. Its performance as supercapacitor electrode was investigated. Additive-free paper-like Ti_3C_2 can yield the volumetric capacitance of 350 F/cm^3 in KOH electrolyte [26], and Ti_3C_2 with binder and carbon black can yield the capacitance of 415 F/cm^3 in H_2SO_4 electrolyte [27]. In this paper, Ti_3C_2 was fabricated and its supercapacitive performance with/without carbon black in KOH electrolyte was investigated.

2 Experimental methods

Ti_3AlC_2 powders (98 wt% pure, –200 mesh) were made from the mixture of TiH_2, Al, and TiC at 1450 ℃ for 2 h in Ar atmosphere [28]. 2D Ti_3C_2 was produced by immersing Ti_3AlC_2 in 49% HF (Aladdin Reagent, China) at 60 ℃ for 24 h followed by washing with deionized water for several times. Finally Ti_3C_2 powders were centrifugally separated from the obtained suspension and dried in vacuum at 80 ℃.

X-ray diffraction (XRD) patterns of the as-fabricated powders were obtained with a diffractometer (Bruker AXS Co., Germany) using Cu Kα radiation. A field emission scanning electron microscope (FESEM; Hitachi, S4800, Japan) was used to characterize the microstructure of the as-prepared powders. Nitrogen sorption isotherm measurements were performed by an automatic gas adsorption analyzer (Autosorb-iQ-MP, Quantachrome, USA) at 77 K. The specific surface area (SSA) was calculated by Brunauer–Emett–Teller (BET) method.

Galvanostatic charge/discharge cycling and cyclic voltammetry (CV) tests were performed by a CSCT supercapacitor test system (Arbin, USA). Electrochemical impedance spectroscopy (EIS) was tested by a potentiostats-electrochemistry work station (Parstat 2273, Princeton Applied Research). Two types of working electrodes were prepared and labeled with Electrode-I and Electrode-II, respectively. Electrode-I was 95 wt% MXene and 5 wt% polytetrafluoroethylene (PTFE); Electrode-II was 85 wt% MXene, 10 wt% carbon black (CB, BP2000, Cabot Corporation, USA), and 5 wt% PTFE. The mixed slurries were pressed under a pressure of 10 MPa to completely adhere together as a disc with diameter of 13 mm and thickness of 0.15 mm. Finally, the electrodes were dried at 120 ℃ in vacuum for 4 h. Both Electrode-I and Electrode-II were assembled into symmetric supercapacitor devices and labeled as SC-1 and SC-2, respectively. The supercapacitive performance of SC-1 and SC-2 was characterized by three-electrode cells in 3 M KOH electrolyte.

3 Results and discussion

3.1 Characterization of Ti_3C_2

Figure 1(a) shows the XRD patterns of Ti_3AlC_2 and Ti_3C_2 MXene. During etching process, Ti_3AlC_2 was exfoliated and Ti_3C_2 MXene with low content of TiC

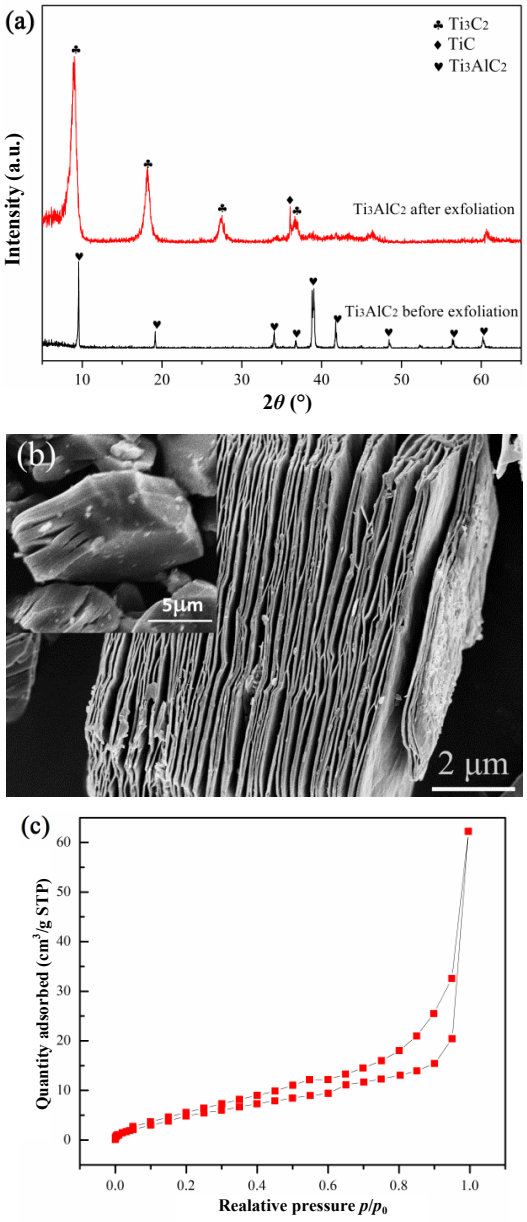

Fig. 1 (a) XRD patterns of Ti_3AlC_2 and Ti_3C_2 MXene; (b) SEM images of Ti_3C_2 MXene with 2D structure, and the inset is the SEM image of Ti_3AlC_2 before exfoliation; and (c) N_2 sorption isotherm of Ti_3C_2.

impurity was obtained. Figure 1(b) shows the FESEM image of the as-synthesized 2D Ti_3C_2. The original Ti_3AlC_2 grains (shown in the inset of Fig. 1(b)) were fully exfoliated and 2D Ti_3C_2 was formed with thickness of ~40 nm [15,21]. The N_2 sorption isotherm of the as-synthesized Ti_3C_2 is shown in Fig. 1(c). The shape of hysteresis loop indicates slit-shaped mesopores. The SSA calculated from BET equation is 22.35 m^2/g.

3. 2 Electrochemical properties

Figure 2 shows the galvanostatic charge/discharge curves of the supercapacitors at different current density. The charge/discharge curves of both SC-1 and SC-2 are almost isosceles triangle, which indicate a good reversibility of SC-1 and SC-2. The capacitance of SC-2 is 71.2 F/g at the current density of 2.5 A/g, corresponding to volumetric specific capacitance of 119.8 F/cm^3, which is higher than that of graphite oxide (110 F/cm^3) [29]. Figure 3 shows the capacitance decay with increasing discharge current density. The capacitance of SC-2 retains 60.4 F/g at the current density of 5 A/g. This indicates the electrodes of SC-2 possess the good conductivity and have good interfacial contact with electrolyte, which provide fast ion transport channels for KOH electrolyte. The capacitance of SC-2 is obviously larger than that of SC-1. Thus, it can be concluded that the addition of carbon black in Ti_3C_2 MXene can significantly improve the performance of supercapacitors. Normally, because of the 2D structure, Ti_3C_2 has obvious preferred orientation. Due to the pressure exerted during the electrode fabrication process, most Ti_3C_2 sheets are lying parallel to the current electrode surface, namely, perpendicular to the direction of ion diffusion, which is unfavorable for the diffusion of electrolyte ions. However, if some carbon black particles are added and located between Ti_3C_2 2D sheets, the preferred orientation is resisted, and thus more ion diffusion channels are generated by the random orientation of 2D Ti_3C_2, especially for those Ti_3C_2 sheets parallel to the direction of ion diffusion. Therefore, the addition of carbon black can greatly increase ion conductivity. This explains the better performance of SC-2.

The cyclic voltammograms (CV) at scan rate of 1 mV/s are presented in Fig. 4. Both CV curves are similar to rectangles and have good symmetry. Thus the supercapacitors are typical electrochemical capacitors.

The impedance spectra are shown in Fig. 5. From

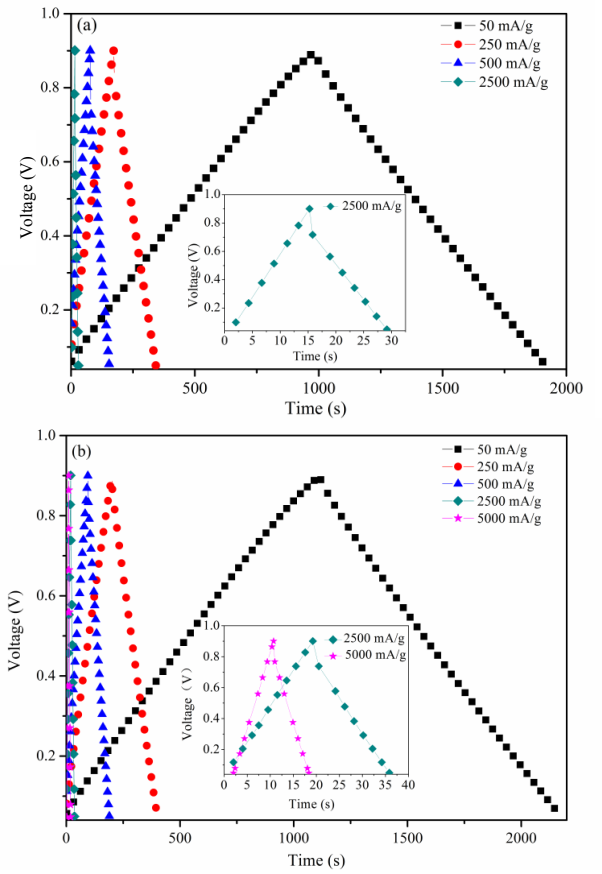

Fig. 2 Galvanostatic charge/discharge curves of the supercapacitors at different current density: (a) SC-1; (b) SC-2.

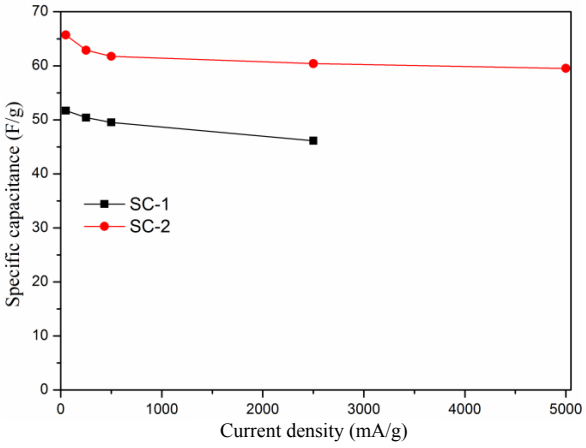

Fig. 3 Specific capacitance of Ti_3C_2-based electrodes at various current densities.

the inset, equivalent resistance of SC-1 and SC-2 devices can be calculated to be 16.7 Ω and 3.5 Ω, respectively. It is clear that Ti_3C_2 with carbon black electrode yields smaller cell resistance and higher capacitance than pure Ti_3C_2 electrode.

A capacitance retention test was performed by

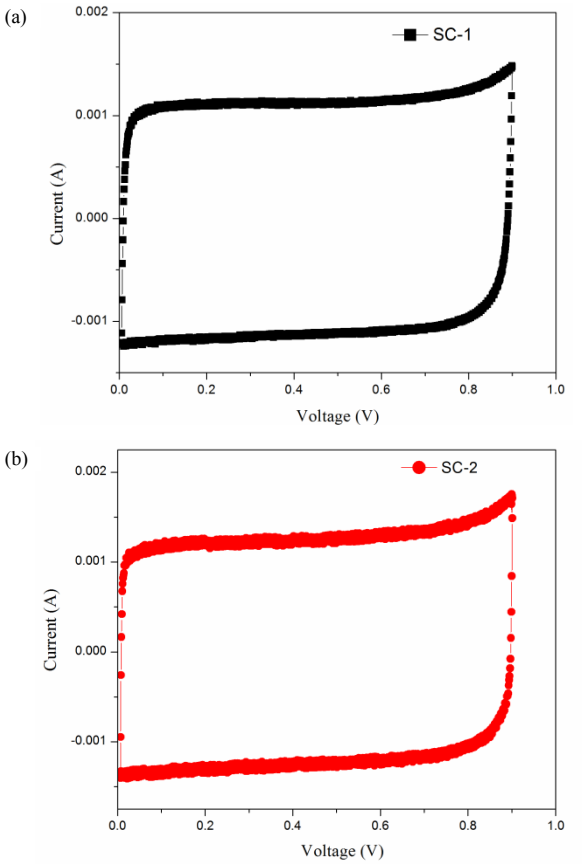

Fig. 4 Cyclic voltammograms curves at 1 mV/s for the Ti_3C_2-based electrodes: (a) SC-1; (b) SC-2.

galvanostatic cycling at 2.5 A/g and the results are showed in Fig. 6. There is almost no degradation in performance of SC-1 after 1000 cycles. Although the capacitance of SC-2 decays with increasing cycle numbers in the beginning cycles, the performance holds steady after 800 cycles, and remains 94.2% of the maximum capacitance. SC-2 still has a good cycling stability and can deliver the high volumetric capacity of 112.9 F/cm^3 after 1000 cycles.

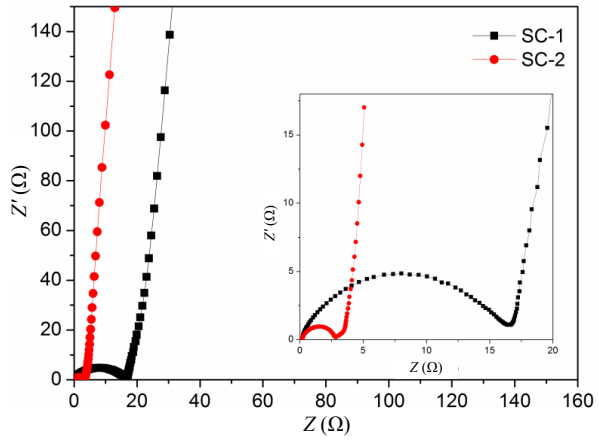

Fig. 5 Nyquist plots of Ti_3C_2-based supercapacitors.

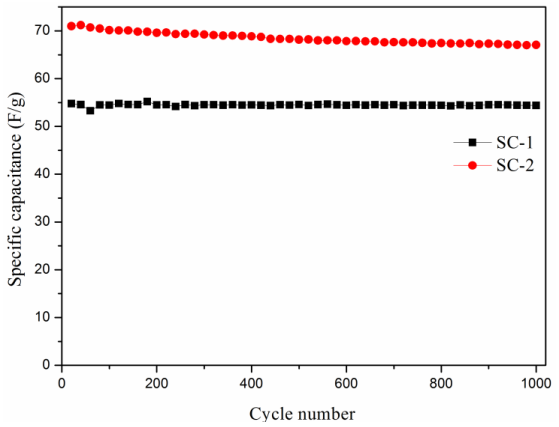

Fig. 6 Capacitance retention test of Ti_3C_2-based supercapacitors.

4 Conclusions

Ti_3C_2 with SSA of 22.35 m^2/g was used to prepare supercapacitors. A volumetric capacitance of 119.8 F/cm^3 has been achieved at the current density of 2.5 A/g. It has a good cycling stability and can deliver a volumetric capacity of 112.9 F/cm^3 after 1000 cycles. Carbon black addition in Ti_3C_2 can avoid the preferred orientation of Ti_3C_2, increasing ion diffusion channel and reducing the diffusion resistance of ion. Equivalent resistance was decreased from 16.7 Ω to 3.5 Ω.

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